

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Art Unit: 1723

Pickford et al

Application number 10/591,793

Examiner: William Leader

Filing Date: 09/06/2006

Title: METAL IMPLANTS

DECLARATION PURSUANT TO 37 CFR S 1.132

1. I, Andrew Derek Turner, have extensive knowledge of and experience with chemistry, particularly inorganic chemistry, ion-exchange processes, and electrochemistry. I obtained a D Phil in chemistry from Oxford University, in the UK, in 1977. Since around 1981 I have worked on the applications of ion exchange and electrochemistry, initially as part of and later leading a team of scientists and engineers that at the outset formed a department within AEA Technology plc and then Accentus plc, based at Harwell in Oxfordshire, UK, and from 2003 to 2009 I provided consultancy services through a separate company, Alchimista Consulting Ltd, in Abingdon, Oxfordshire, UK. I am currently working for the applicant company. I am named as one of the inventors of the present application.

2. I have carried out experimental tests to compare the effects of anodising in accordance with US 5 211 832 (Cooper) examples 6 and 7, and anodising in accordance with one aspect of the present invention (referred to as the Agluna[®] process). The results were as follows:

Practising Examples 6 & 7 of Cooper US Patent No. 5,211,832**Experimental**

In accordance with Cooper's Examples 6 and 7, the experimental procedure followed Example 1 of Cooper, steps 1-13 (col 4 l. 40 to col 5 l. 25) was followed, apart from the boiling step. A solution of 1 part (10 ml) aqueous 85% H₃PO₄ (non-boiled) was added to 9 parts (90 ml) propylene carbonate and placed in a sealed flask. A titanium 99.99+%, 25x25 mm, 0.025 mm thick (as rolled) sample was imaged using a microscope. The sample was then ultrasonically cleaned (i) using acetone and rinsed with de-ionized water (ii) using HNO₃ and rinsed with ionized water. The sample was connected, and a portion of the sample area was placed in the electrolyte mixture. The vessel was sealed using Parafilm and electrical tape. The power supply was set to a 1 mA/cm² current limit and the voltage to 100V. Power was applied and the sample anodized for ~6 hours with stirring in accordance with examples 6 and 7 (col 6 l. 25). Current, charge and voltage were data logged throughout the process. The applied voltage was stepped down in 5V and then 10V steps to examine the zero current point. The sample was then removed from the electrolyte, rinsed in deionized water, and the surface inspected using a microscope.

Comparison

For comparison, a titanium alloy (Ti6Al4V) sample was treated by an anodising process described in US 10/591,793, anodising in aqueous phosphoric acid up to 100 V, with a current limit of 5 mA/cm², for 2 hours. Other tests were carried out with a current limit of 10 mA/cm², for 2 hours. The resulting surface is substantially the same in each case. The current initially increases, but after a couple of minutes, when the voltage reaches 100 V, the current drops to a stable low value which is much less than that set by the current limit. The current remains low for the remaining two hours. These conditions are collectively referred to below as the Agluna[®] process.

Microscopy

In each case both before and after the anodising treatment the sample was imaged by an optical microscope using a x100 objective lens. In each case the optical microscope was used to produce both a conventional image and a Nomarski interference contrast image.

In addition, after each sample had been anodised it was then imaged by a scanning electron microscope, to obtain greater magnification.

Results

Pre Cooper treatment

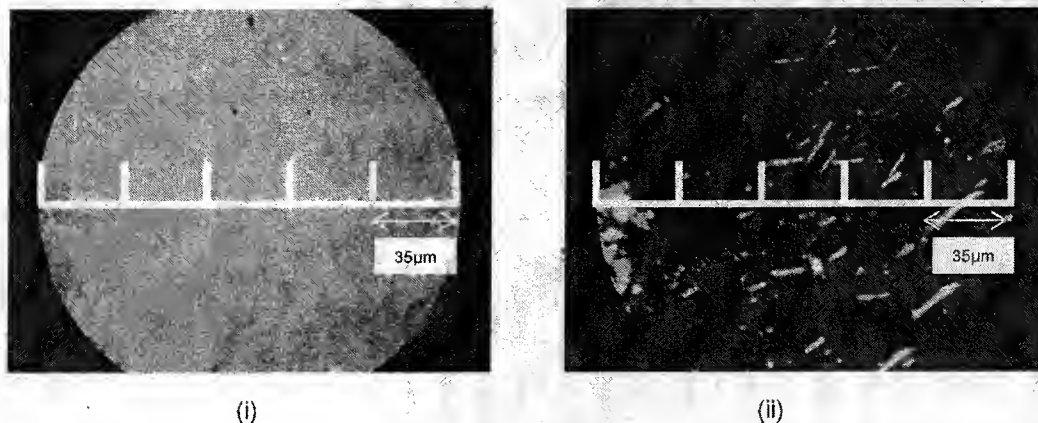


Figure 1 Microscope image of Titanium 99.99+% sample before Cooper treatment:
(i) Image (ii) Nomarski interference contrast image

The sample's finish is described as 'as rolled' by the manufacturer and the images clearly show a surface roughness most likely associated with the manufacturing / rolling process.

Post Cooper Treatment

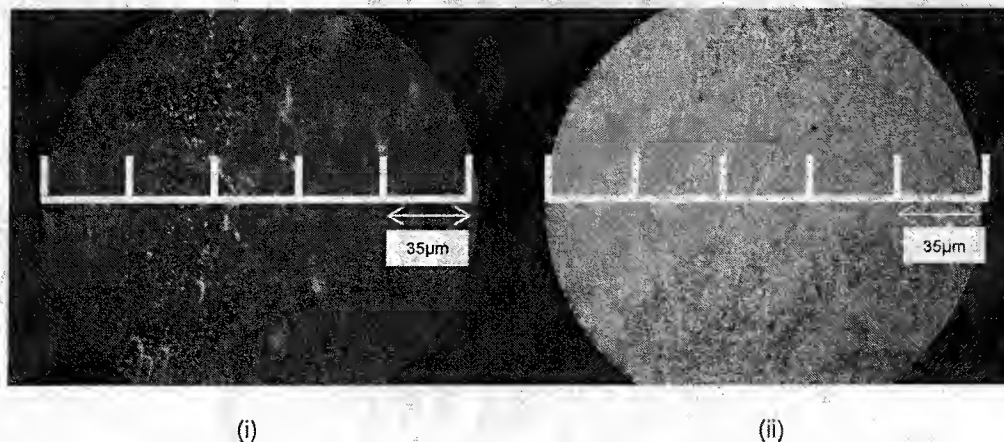


Figure 2 Microscope image of Titanium 99.99+% sample after Cooper treatment
(i) Image (ii) Nomarski interference contrast image

The sample surface finish, after processing, shows a blue anodised film (Figure 2(i)) and evidence of the initial surface roughness due to manufacture / machining marks.

There are no visible pits.

Pre Agluna® Treatment

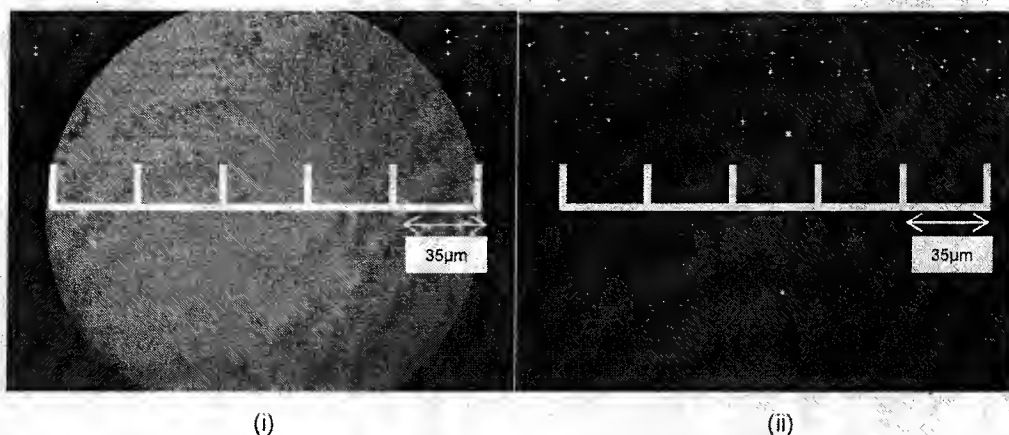


Figure 3 Microscope image Titanium alloy (Ti6Al4V) polished surface
(i) Image (ii) Nomarski interference contrast image

The sample finish is described as 'mechanically polished' by the manufacturer and the images clearly show a moderate to low surface roughness most likely associated with the manufacturing / polishing. This shows up as stripes in the higher magnification images obtained by SEM (see especially Figure 7 below).

Post Agluna® Treatment (a)

100V for 2 hours, and 5 mA/cm² current limit

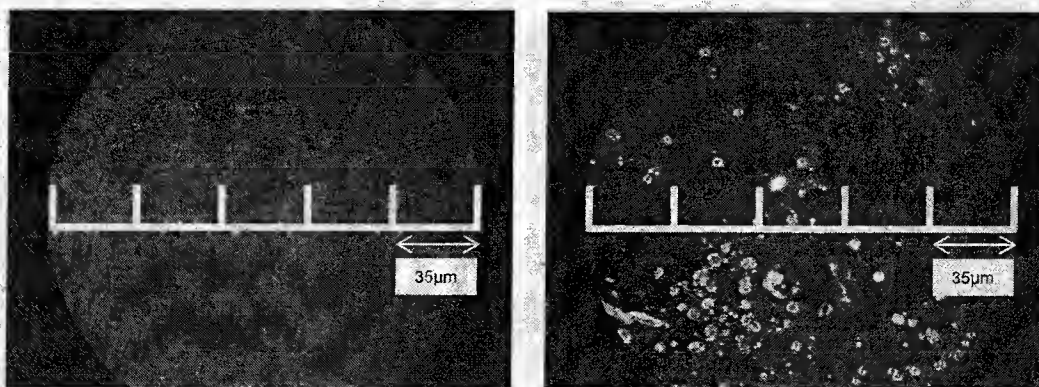


Figure 4 Microscope image of Titanium alloy (Ti6Al4V) polished surface after Agluna® Treatment
(i) Image (ii) Nomarski interference contrast image

The Agluna® treated samples (Figure 4 (i) & (ii)) clearly show the presence of a coloured anodised film following the treatment, with the addition of pits in the surface. The pits are visible in these X100 microscope images, and appear to be of diameter up to about 5 µm.

By way of example, comparing Figure 4(ii) to Figure 2(ii) it can clearly be seen that the Cooper process does not produce discrete pits with the features and dimensions that are produced according to the Agluna process.

Post Agluna® Treatment (b)

100V for 2 hours, and 10 mA/cm² current limit

By way of further example Figure 5 is an optical microscope image of a titanium alloy sample surface after an Agluna® treatment at 100V for 2 hours and with a 10 mA/cm² current limit. The image was taken with a different microscope and illumination to that used in Figures 1-4, but again using a x100 objective lens. The surface clearly shows the presence of an anodised film following the treatment, from the blueish colour, with the addition of pits in the surface. The pits are visible in these microscope images, and appear to be of diameter up to about 5 µm. This is confirmed by SEM imaging, as shown in Figure 8 below, showing that the pits have dimensions of ~1-5 µm.

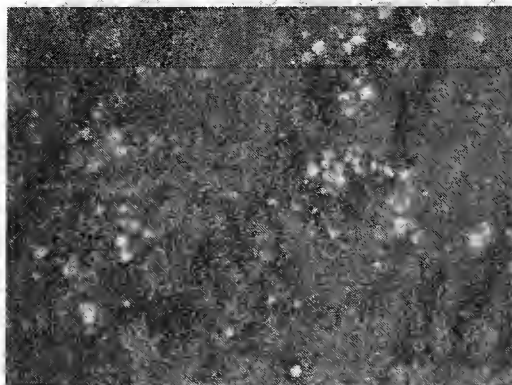


Figure 5 Microscope image of Titanium alloy (Ti6Al4V) polished surface after Agluna Treatment

Scanning Electron Microscope imaging (SEM)

Inspection using SEM – Each anodised sample was then inspected using a scanning electron microscope, to view the surface at greater magnification than with an optical microscope.

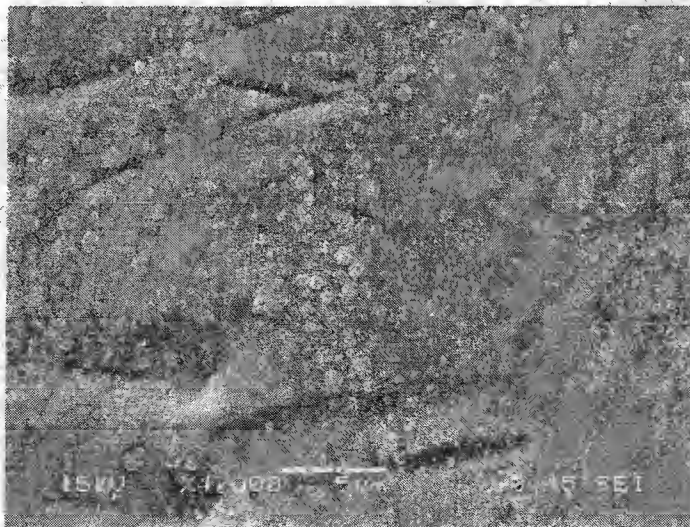


Figure 6 SEM image of Cooper treated sample

The SEM image (Figure 6) of a surface treated according to Cooper shows that a substantial proportion of the surface has a 'patterned' appearance with dots or patches of diameters typically 0.5 μm or less.

This is very different from an Agluna[®] treated surface where there are large and prominent pits filled with soft material. Figures 7 and 8 show examples of an Agluna[®] treated surface; they show SEM images (x2000 magnification, 30 and 20 μm graticules respectively) of two different titanium alloy samples, each processed at 100V for 2 hours with a current limit of 10 mA/cm², that is to say Agluna[®]-treated surfaces. The SEM image of Figure 8 shows the same sample as shown in Figure 5 above.

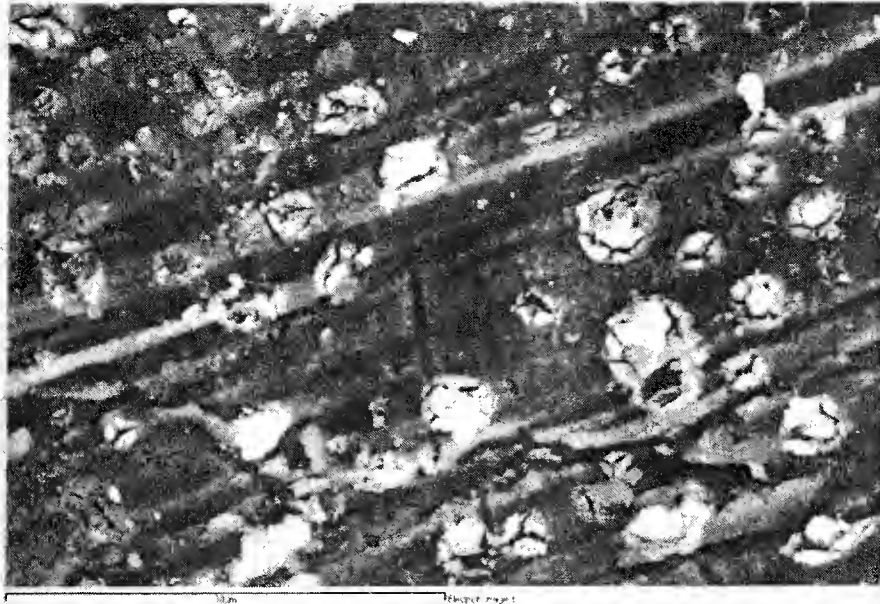


Figure 7 SEM of Agluna[®] treated sample

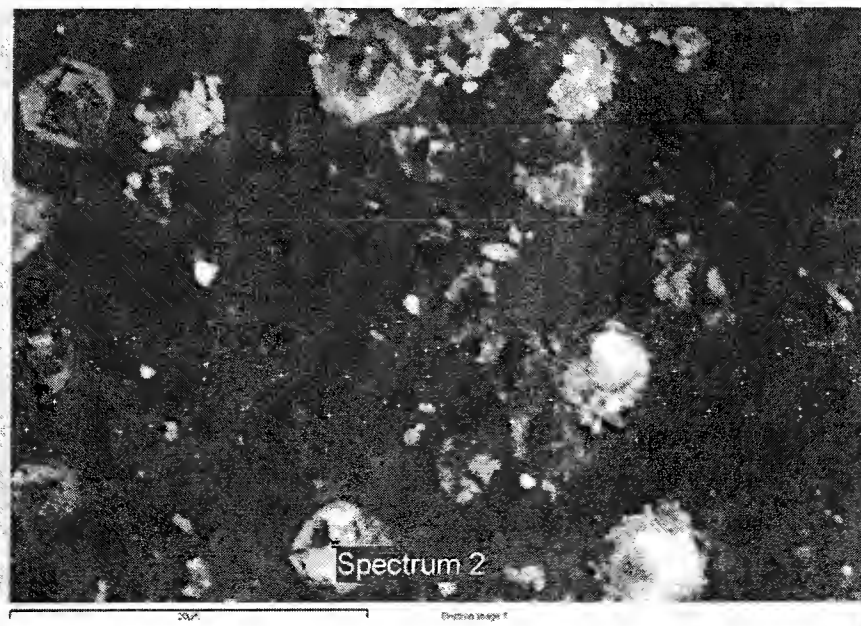


Figure 8 SEM image of Agluna[®] treated sample (same sample as imaged in Figure 5)

The diagonal grooves visible in Figures 7 and 8 are machining and polishing lines across the titanium surface.

Pits characteristic of the Agluna® process are clearly observed in Figure 7 and 8 across the surface of each sample, and as is evident from the graticules (30 µm and 20 µm graticules respectively) at the bottom of the images, are typically several microns in diameter. In each case the pits are clearly visible, and are far larger and far less abundant than the dots or patches formed by the Cooper process (shown in Figure 6).

3. I declare that all of the above statements made of my own knowledge are true and all statements made on information and belief are believed to be true. I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. s.1001), and may jeopardize the validity of the application or any patent issuing thereon.

Date: 18th August 2011

By: Andrew Derek Turner

Andrew Derek Turner